

## PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO  
THE PREPARATION OF 1,4-BUTANEDIOL

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of 1,4-butanediol from *p*-butyrolactone. 1,4-Butanediol is used for preparing polyesters.

Processes for preparing 1,4-butanediol are already known. As well as a number of older syntheses, for example based on acetylene/formaldehyde or 1,4-dihalogenobutane, processes for preparing 1,4-butanediol by hydrogenation (hydrogenolysis) of *p*-butyrolactone have recently been described. In these processes 1,4-butanediol is obtained, partly with very good yields.

However, the processes require the use of copper oxide/chromium oxide (Adkins) catalysts which are generally very sensitive to water and extremely sensitive to acids. This means that the starting materials used for hydrogenation must be made completely water-free and the acid impurities frequently obtained in the preparation of *p*-butyrolactone must also be removed, which makes the processes complicated and uneconomical.

However, the cheapest methods of preparing *p*-butyrolactone, for example by hydrogenation of maleic anhydride or maleic acid, lead to products containing rather large quantities of water and organic acid, especially propionic acid, butyric acid, unreacted residual maleic acid and, especially, succinic acid. Consequently, this *p*-butyrolactone cannot be further reacted to yield 1,4-butanediol by using the conventional Adkins catalysts known for ester hydrogenations, especially lactone hydrogenations, since these catalysts,

which are known to operate well in a neutral medium, would be deactivated irreversibly after short operation times.

The present invention provides a process for preparing 1,4-butanediol, from *p*-butyrolactone, which comprises hydrogenolysing *p*-butyrolactone, optionally still containing water or a carboxylic acid or a mixture of two or more thereof, in the presence of a copper oxide/chromium oxide catalyst pretreated with hydrogen, outside the hydrogenolysis zone.

*p*-Butyrolactone still containing some portions of water and/or organic acids, for example, propionic acid, butyric acid, maleic acid and especially succinic acid may, consequently, be hydrogenated in a simple and economic manner yielding 1,4-butanediol, and no removal of the water or acid prior to hydrogenolysis is needed. Thus, the steps of extraction, distillation, neutralisation and/or drying required in a previous processes to remove water and/or acids, become unnecessary.

The catalyst used is advantageously a copper oxide/chromium oxide catalyst containing from 30 to 50% of CuO, 30 to 50% of Cr<sub>2</sub>O<sub>3</sub> (the rest being H<sub>2</sub>O), especially, containing from 42 to 48% of CuO, 42 to 48% of Cr<sub>2</sub>O<sub>3</sub> (the rest being H<sub>2</sub>O) for example a conversion Adkins catalyst, the percentages being by weight and relating to the catalyst before hydrogen treatment.

Copper oxide/chromium oxide catalysts containing additionally rhenium and/or manganese in elementary or bound form are preferably used.

The present invention also provides such a copper oxide/chromium oxide catalyst which has been pretreated with hydrogen.

The catalysts treated with hydrogen prior to use in this manner show hardly any loss of activity even when used repeatedly; in contrast, known copper oxide/chromium oxide catalysts are deactivated in the presence of acids, as can generally be seen by the strong blue-green natural colour of the reaction solutions.

2 The preliminary treatment of the catalysts according to the invention moreover surprisingly considerably improves the ability of separating the catalysts, for example when used in discontinuous hydrogenation plants, in comparison to that of normal untreated Adkins catalysts.

5 The process process of the invention also has the advantage of producing 1,4-butanediol practically free from acids from  $\gamma$ -butyrolactone containing carboxylic acids.

10 The copper/chromium catalysts pretreated according to the invention moreover have the advantage that the formation of tetrahydrofuran in the reduction of  $\gamma$ -lactone can be practically ignored. 1,4-Butanediol is formed generally with very high selectivity.

15 It is moreover surprising that the advantages of the process of the invention reside in the preliminary treatment of conventional Adkins catalysts with hydrogen. In the literature it has always been pointed out that reduced forms of copper/chromium oxide catalysts are considerably less active than the unreduced ones during liquid phase hydrogenations wherein Adkins catalysts are used.

20 The preliminary treatment of the commercial Adkins catalysts with hydrogen is generally carried out at a temperature of from 50 to 250°C, for example, by filling a glass tube with the Adkins catalyst and by passing hydrogen through. In this process nitrogen is advantageously admixed with the hydrogen. The proportion of hydrogen to nitrogen may vary within wide limits. A mixture of 9 parts by volume of nitrogen and 1 part by volume of hydrogen has proved advantageous. The time of the preliminary treatment suitably ranges from 15 minutes to 6 hours. The catalysts are moreover suitably submitted to a secondary treatment with carbon dioxide, generally by cooling the catalyst treated with hydrogen in a CO<sub>2</sub> current.

25 When using rhenium-containing catalysts, a normal copper/chromium catalyst may be impregnated with an aqueous solution of rhenium heptoxide and then treated with hydrogen.

30 For carrying out the conversion of lactone to 1,4-butanediol in optimum manner, hydrogenolysis of  $\gamma$ -butyrolactone is generally performed at elevated pressure and temperature.

35 The reaction temperature suitably is in the range of from 50 to 300°C, preferably in the range of from 150 to 250°C.

40 The hydrogen pressure is suitably in the range of from 50 to 300 bars, preferably of from 100 to 250 bars.

Suitably, the amount of hydrogen used for the hydrogenolysis of the  $\gamma$ -butyrolactone is larger than the stoichiometrical amount. Unreacted hydrogen may be recycled to the reaction medium as a circulating gas. The reaction may be carried out continuously or discontinuously.

45 Technically pure hydrogen is generally used. Admixture of the hydrogen with an inert gas such, for example, as nitrogen, however, does not disturb the reaction.

50 The catalysts are suitably used in powdered form, but they may also be used in a tabletted form and/or in admixture with inert materials. Suitable inert materials, for example, are active carbon, silicon dioxide and aluminium oxides.

55 If rhenium or manganese are used as co-catalysts, their proportion as elements in the total mass of the catalytically active substances, i.e. without the support, suitably is in the range of from 0.01 to 10% by weight, the percentages relating to the catalyst before hydrogen treatment.

60 The co-catalysts may be incorporated into the Adkins catalysts during their preparation or be admixed thereto at a later stage, for example, by simple mechanical means.

65 The co-catalysts may be used in elementary form or in the form of their compounds, for example as nitrates, carbonates or, especially, as oxides or a mixture of two or more thereof. An addition of elementary rhenium is especially advantageous.

70 The reaction time in the conversion to 1,4-butanediol is generally in the range of from 5 minutes to 6 hours. When working discontinuously for example, it may range from about 3 to 5 hours.

75 Powdered catalysts may be filtered off when the reaction is terminated and be reused, without a notable loss of activity.

80 When working continuously, for example, in the trickling phase, tabletted catalysts are suitably used.

85 For carrying out the reaction, conventional ester hydrogenation solvents, for example dioxan, ether or methyl cyclohexane, may be used. However, the reaction may also be performed without using a solvent.

90 The acid content of the  $\gamma$ -butyrolactone to be hydrogenated may be, for example, in the range of from 0.01 to 25% by weight preferably of from 1 to 10% by weight, especially of from 2 to 8%.

95 The water content of the mixture to be hydrogenated may be, for example, in the range of from 0 to 26% by weight, preferably of from 1 to 10%, especially of from 2 to 7% by weight.

100 The quantity of catalyst required for

hydrogenation of *p*-butyrolactone is generally in the range of from 0.5 to 25°, by weight of the quantity of lactone.

5 The following method has proved advantageous for carrying out the process of the invention:

10 *p*-butyrolactone, still containing water and/or organic carboxylic acids is placed in a high pressure autoclave, the catalyst is added and hydrogen is introduced by pressure. The reaction mixture is heated rapidly to the desired reaction temperature and allowed to react until no more pressure decrease is observed. The reaction product is rapidly cooled, the pressure is released and the reaction mixture is worked up. The reaction mixture separated from the catalyst is distilled by fractionation.

20 The following Examples illustrate the invention, the percentages being by weight:

#### EXAMPLE 1:

10 g of a commercial copper/chromium oxide catalyst containing 44 to 46% of CuO, 43 to 46% of Cr<sub>2</sub>O<sub>3</sub> and 5.1% of manganese dioxide (the remainder being H<sub>2</sub>O) being admixed with 1% of elementary rhenium and then pretreated with hydrogen, were added to a solution 0.25 mole (21.5 g) of *p*-butyrolactone in 90 g of dioxan containing 6 g (5%) of succinic acid and 2.55 g of H<sub>2</sub>O (2.5%) and hydrogenolysed in a shaking autoclave for a period of 6 hours, at a temperature of 25°C and under a hydrogen pressure of 170 bars.

35 When the reaction was terminated, 107 g of water-clear reaction mixture was obtained containing, besides dioxan, 19.8% (21.2 g) of 1,4-butanediol corresponding to a yield of 94%. The presence of succinic acid could no longer be detected.

#### EXAMPLE 2

10 g of a commercial catalyst based on copper/chromium oxide (containing from 44 to 46% of CuO, 43 to 46% of Cr<sub>2</sub>O<sub>3</sub> and 5.1% of MnO<sub>2</sub>, as in Example 1, but no rhenium) which had been treated with hydrogen for 4 hours at 160°C, were added to 120 g of a mixture comprising 18% of *p*-butyrolactone (0.25 mole), 75% of dioxan as solvent, 5% of succinic acid, and 2% of water, and the reaction mixture was placed into a shaking autoclave. Hydrogen was added until a pressure of 170 bars was attained, and the reaction mixture was rapidly heated to a temperature of from 225 to 230°C. After a reaction time of 3 hours, 102 g of a clear, slightly grey reaction solution was obtained.

60 The solution contained, besides 15% of 1,4-butanediol, 2.9% of unreacted *p*-lactone and about 0.8% of succinic acid.

The yield of butanediol was about 70% of the theoretical yield.

#### COMPARATIVE EXAMPLE

120 g of a solution as in Example 1 were hydrogenolysed with 10 g of a commercial untreated catalyst based on copper/chromium oxide (composition as in Example 2) in an analogous manner to Example 1. 105 g of a slightly turbid, bluish-green reaction solution were obtained containing only 9% of 1,4-butanediol (44% of the theoretical yield).

#### EXAMPLE 3

11.8 g of the catalyst used in Example 1, which had been filtered off and was still slightly wet, were reused for hydrogenolysis with 120 g of reaction solution as described in Example 1.

106 g of a clear solution were obtained, containing 19.6% of 1,4-butanediol corresponding to about 93% of the theoretical yield.

#### EXAMPLE 4

4.5 g of the catalyst based on copper/chromium/manganese oxide and rhenium, pretreated with hydrogen, as described in Example 1 were added to a mixture of 86 g of *p*-butyrolactone (1 mole) and 3.6 g of succinic acid and the reaction mixture was introduced into a magnetic type lifting stirring autoclave having a volume of 0.5 litre. Hydrogen was introduced until a pressure of 120 bars was attained, the reaction mixture was rapidly heated to 220°C, and allowed to react for a period of 4 hours.

When the reaction was terminated and the catalyst separated by filtration, 90.5 g of a clear reaction solution were obtained containing 96% (86 g) of 1,4-butanediol. Succinic acid could no longer be detected.

#### EXAMPLE 5

5 g of a commercial catalyst based on copper and chromium oxide (portion of metal: from 33 to 34% of Cu, from 29 to 30% of Cr; the remainder: oxygen and some H<sub>2</sub>O) which was admixed with 1.5% of elementary rhenium and then pretreated with hydrogen, were added to 120 g of the mixture described in Example 1, but containing instead of 5% of succinic acid, 4.5% of succinic acid and 0.5% of maleic acid, and the reaction mixture was hydrogenolysed under the reaction conditions indicated in Example 1. After a reaction time of 2.5 hours, 103 g of a clear reaction solution were obtained containing 20.9 g of 1,4-butanediol.

Free organic acid could no longer be detected at the end of the reaction.

## WHAT WE CLAIM IS:—

1. A process for preparing 1,4-butanediol which comprises the hydrogenolysis of  $\gamma$ -butyrolactone in the presence of a copper oxide/chromium oxide catalyst which has been pretreated with hydrogen outside the hydrogenolysis zone.
2. A process as claimed in claim 1, wherein the catalyst contains from 30 to 50% by weight of  $\text{CuO}$  and from 30 to 50% by weight of  $\text{Cr}_2\text{O}_3$ , the rest being water and the percentages relating to the catalyst before hydrogen treatment.
3. A process as claimed in claim 2, wherein the catalyst contains from 42 to 48% by weight of  $\text{CuO}$  and from 42 to 48% by weight of  $\text{Cr}_2\text{O}_3$ , the rest being water, and the percentages relating to the catalyst before hydrogen treatment.
4. A process as claimed in any one of claims 1 to 3, wherein the catalyst has been pretreated with hydrogen at a temperature in the range of from 50 to 250°C.
5. A process as claimed in any one of claims 1 to 4, wherein the catalyst has been pretreated with hydrogen for a period of time from 15 minutes to 6 hours.
6. A process as claimed in any one of claims 1 to 5, wherein the catalyst has been pretreated with a mixture of hydrogen and nitrogen.
7. A process as claimed in claim 6, wherein the ratio of nitrogen to hydrogen is substantially 9:1.
8. A process as claimed in any one of claims 1 to 7, wherein the catalyst has been subjected to a secondary treatment with  $\text{CO}_2$ .
9. A process as claimed in any one of claims 1 to 8, wherein the catalyst contains additionally manganese and/or rhenium, in elementary and/or in bound form, as co-catalyst.
10. A process as claimed in claim 9, wherein the cocatalyst comprises a manganese or rhenium nitrate, carbonate or oxide or a mixture of two or more thereof.
11. A process as claimed in claim 9, wherein the co-catalyst comprises elementary rhenium.
12. A process as claimed in any one of claims 9 to 11, wherein the amount of manganese or rhenium as elements in the total mass of catalytically active substance i.e. without support, is in the range of from 0.01 to 10 % by weight, the percentages relating to the catalyst before hydrogen treatment.
13. A process as claimed in any one of claims 9 to 12, wherein the co-catalyst has been incorporated with the copper oxide/chromium oxide catalyst before the pretreatment with hydrogen.
14. A process as claimed in any one of claims 1 to 13, wherein the  $\gamma$ -butyrolactone starting material contains from 0 to 20 % by weight of water.
15. A process as claimed in claim 14, wherein the  $\gamma$ -butyrolactone contains from 1 to 10 % by weight of water.
16. A process as claimed in claim 15, wherein the  $\gamma$ -butyrolactone contains from 2 to 7 % by weight of water.
17. A process as claimed in any one of claims 1 to 16, wherein the  $\gamma$ -butyrolactone starting material contains from 0.1 to 25% by weight of carboxylic acid component.
18. A process as claimed in claim 17, wherein the  $\gamma$ -butyrolactone contains from 1 to 10% by weight of carboxylic acid component.
19. A process as claimed in claim 18, wherein the  $\gamma$ -butyrolactone contains from 2 to 8% by weight of carboxylic acid component.
20. A process as claimed in any one of claims 1 to 19, wherein the hydrogenolysis reaction is carried out at a temperature of from 50 to 300°C.
21. A process as claimed in claim 20, wherein the reaction is carried out at a temperature in the range of from 150 to 250°C.
22. A process as claimed in any one of claims 1 to 21, wherein the hydrogenolysis reaction is carried out under a hydrogen pressure of from 50 to 300 bars.
23. A process as claimed in claim 22, wherein the reaction is carried out under a hydrogen pressure of from 100 to 250 bars.
24. A process as claimed in any one of claims 1 to 23, wherein excess hydrogen is used in the hydrogenolysis reaction.
25. A process as claimed in any one of claims 1 to 24, wherein the hydrogenolysis reaction is carried out for a period of time from 5 minutes to 6 hours.
26. A process as claimed in any one of claims 1 to 25, wherein the hydrogenolysis reaction is carried out in the presence of a solvent comprising dioxan, ether or methylcyclohexane.
27. A process as claimed in any one of claims 1 to 26, wherein the catalyst is present in an amount of from 0.5 to 25 % by weight, based on the weight of  $\gamma$ -butyrolactone.
28. A process as claimed in claim 1,

carried out substantially as described in any one of the Examples 1 to 5 herein.

29. 1,4-Butanediol, whenever prepared by a process as claimed in any one of claims 1 to 28.

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